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14. ABSTRACT

We have formulated composites of lead (II) tetrakis (4-cumylphenoxy) phthalocyanine (PbTCPc) doped into nematic liquid crystal (LC), 40-pentyl-4-biphenylcarbonitrile (5-CB), that has received a 90° twisted alignment and investigated the nonlinear transmission properties using both pulsed (Nd:YLF 524nm, 5 ns) and cw (532 nm) lasers. In the nanosecond regime, this compound is a reverse saturable absorber performing

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Block 13: Supplementary Note

Nonlinear optical transmission of lead phthalocyanine-doped nematic liquid crystal composites for multiscale nonlinear switching from nanosecond to continuous wave

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We have formulated composites of lead (II) tetrakis (4-cumylphenoxy) phthalocyanine (PbTCPc) doped into nematic liquid crystal (LC), 4′-pentyl-4-biphenylcarbonitrile (5-CB), that has received a 90° twisted alignment and investigated the nonlinear transmission properties using both pulsed (Nd:YLF 524 nm, 5 ns) and cw (532 nm) lasers. In the nanosecond regime, this compound is a reverse saturable absorber performing similarly to low-concentration solutions of PbTCPc. Under cw conditions, we observe optically self-activated polarization switching with low threshold input energy. Our results suggest the potential for an all-optical switch working from the nanosecond time scale to cw. © 2009 Optical Society of America

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Nonlinear transmission can be used to protect optical sensors or human eyes from the damage caused by high intensity lasers. Many nonlinear optical processes, such as thermal diffraction [1], molecular reorientation [2,3], multiphoton absorption [4], and reverse saturable absorption (RSA) [5,6], and corresponding materials have been studied. In recent years, organic macromolecules, such as phthalocyanines (Pc) and their metal complexes have been widely studied because their strong RSA effect is promising for nonlinear optical applications in the nanosecond (ns) regime, especially when heavy metal atoms are substituted at the center [7–11], as this increases the population of molecules in the triplet ground state. One major challenge for applications is presented by the multiple time scales of laser sources: materials that work at one time scale are often useless at others. For example, Pc macromolecules work mainly in the ns regime because this is the relevant time scale for intersystem crossing from the singlet to the triplet state. On the other hand, laser-induced polarization switching has been studied in dye-doped nematic liquid crystals (LCs) for passive all-optical switching at the microsecond time scale and above [2,12].

In this work, we have combined these two materials into a composite that takes advantage of each of their beneficial properties in one system. The lead (II) tetrakis (4-cumylphenoxy) phthalocyanine (PbTCPc) was dissolved in a twisted alignment nematic LC, 4′-pentyl-4-biphenylcarbonitrile (5CB). We established this to be an effective process for making an easily fabricated, phase-stable PbTCPc/LC compound nonlinear optical switch. With an appropriate concentration of dye, the devices provided performance comparable to that of dilute solutions of

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PbTCPc in the ns regime [8]. Conversely, the same device exhibited optically activated polarization switching with low threshold energy, suitable for continuous-wave (cw) optical switching.

The nonlinear absorption dye used was lead tetrakis (4-cumylphenoxy) phthalocyanine (PbTCPc, 90%, Aldrich). Roughly 3% by weight PbTCPc was doped into the nematic LC, 4′-pentyl-4-biphenylcarbonitrile (5-CB, 98% pure, Aldrich). The glass window surface was coated with 300 nm of polyvinyl alcohol (PVA, Sigma), and the PVA film was subsequently rubbed unidirectionally to create planar alignment. The cells were prepared using two glass substrates with their alignment layers orthogonal to each other, separated by a 140 μm spacer and a 70 μm spacer for Samples 1 and 2, respectively. When filled with the dye/LC mixture and sealed with epoxy, a 90° twisted alignment PbTCPc-doped nematic LC cell is thus fabricated. Figure 1 shows pictures of Sample 1 and Sample 2, each of which had been stored in air for more than two weeks; the pictures were taken after all the measurements had been done. The lower part of Fig. 1 depicts the 90° twisted alignment of the nematic LC cell.

The nonlinear transmission experiments were performed with a frequency doubled Nd:YLF laser (524 nm), which provides 5 ns width pulses with a repetition rate of 1 Hz. We used two polarizers in series to act as an attenuator for adjusting the incident laser energy; then the input laser was split into two beams, one being employed as a reference and the other focused onto the sample using a 10 cm focal length lens. The reference and transmitted laser energies were collected with a lens and measured simultaneously by two identical photodiodes. The response of the system over the fluence dynamic range of this work has been checked using a glass substrate as a linear reference sample. The linear transmittance was determined by dividing the signal magnitude on the detector photodiode with the sample in the beam and without the sample in the beam at low fluence, which were 0.37 and 0.62 at 524 nm for Sample 1 and Sample 2, respectively, as expected considering the thicknesses of the two samples.

The cw laser measurement setup was similar to the pulsed laser one, except that the sample was placed between two crossed polarizers and the laser was unfocused. The polarization direction of the input laser beam was parallel to the rubbed direction of the incident glass substrate. The transmitted light will be ordinarily rotated 90° by the LC cell, according to the Mauguin theorem. Therefore, the transmission through the analyzer is expected to be at a maximum.

Figure 2 shows the normalized transmittance as a function of input fluence for Sample 1 and Sample 2 for ns pulse measurements. We define the threshold for nonlinear transmission to be the incident fluence for which the transmittance of the film is 50% of the linear transmittance. Thus, the threshold fluence is 40 and 75 mJ/cm^2 for Sample 1 and Sample 2, respectively, which is comparable to the threshold of ~70 mJ/cm^2 observed in PbTCPc solution with 62% linear transmittance when measured by a similar ns 532 nm Nd:YAG laser [8].

It has been discussed that the mechanism of nonlinear transmission for heavy-atom-substituted Pcs in the ns regime can be attributed to the RSA effect from both singlet excited states and triplet states [7–11]. Nonlinear absorption processes for metallophthalocyanines (MPcs) have been studied in detail using five-level models, depicted schematically in Fig. 3 [13]. An electron in the ground state absorbs one photon and is excited to first singlet state S_1 with cross section σ_g. The excited electron may directly absorb another photon and be promoted to a higher singlet excited state S_2 with a cross section σ_s, or can undergo an intersystem crossing transition to the triplet state T_1, before relaxing back to ground state. Subsequently, the electron in the T_1 state may also absorb another photon, thereby occupying a higher

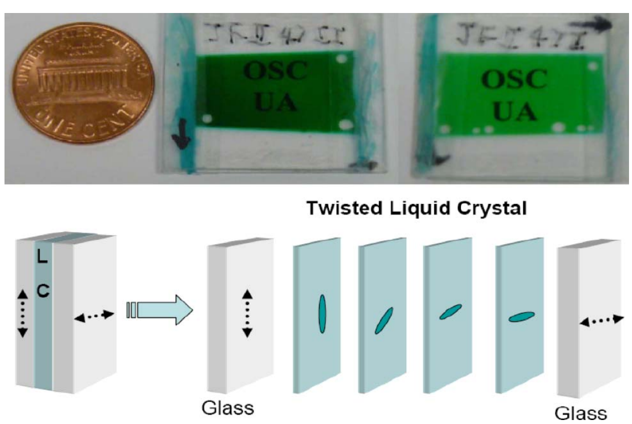

Fig. 1. (Color online) Images of two samples and schematic view of the twist of LC between planar glass windows with orthogonally oriented PVA alignment layers.

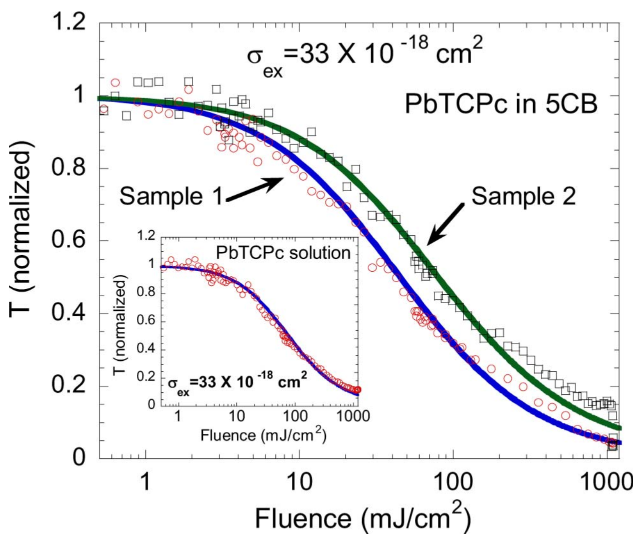

Fig. 2. (Color online) Normalized nonlinear transmission of PbTCPc-doped LC cells, as well as PbTCPc dilute solution (inset), with respective fitting results.

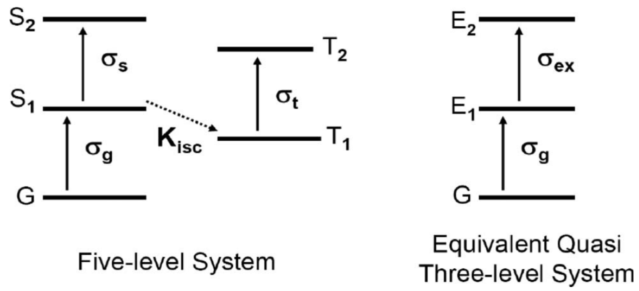

Fig. 3. Schematic diagram of the five-level model and equivalent quasi-three-level model.

triplet state with a cross section σ_t, or decay back to ground state as well. If the weak absorption from the ground states results in a substantial electron population in any of the lowest excited states (S_1 or T_1), and those excited states have larger absorption cross sections than σ_g, an overall decrease in transmittance upon excitation is expected. Consequently, the nonlinear transmission properties are a function of the input fluence as well as pulse duration. For example, if the lifetime for electrons' transition from the S_1 states to T_1 states, i.e., $1/K_{\mathrm{isc}}$, is much longer than pulse width, the contributions of the triplet states to nonlinear absorption can be neglected. If only total pulse fluence is of interest, the quasi-three-level system shown in Fig. 3, which consists of ground state absorption and an equivalent excited state absorption process [13], can be used to describe the nonlinear absorption. The equivalent excited absorption, σ_{ex}, can range from σ_s to σ_t and is finally determined by the lifetimes of the energy levels, the intersystem crossing rate K_{isc}, and the laser pulse width. Although σ_{ex} has no direct physical meaning, it is a convenient parameter for comparing the performance among materials for a given laser system.

Within the three-level approximation, the total pulse fluence F changes with z according to Ref. [13]:

$$\partial F/\partial z = -(\sigma_{\mathrm{ex}} N_0 - (\sigma_g - \sigma_{\mathrm{ex}}) \times [\exp(-F/F_s) - 1] N_0 F_s/F)F; \qquad (1)$$

σ_g is the ground state absorption cross section, which has been determined by linear transmittance measurements of dilute solutions to be $2.0 \times 10^{-18}\,\mathrm{cm}^2$. $F_s = h\nu/\sigma_g$ is the saturation fluence. Therefore, only one unknown parameter, σ_{ex}, must be determined to fit the measurements shown in Fig. 2. For reference, a dilute PbTCPc solution sample with a concentration of 0.43 mg/ml was prepared in a 1 mm cell with a linear transmittance of 62% and limiting threshold of $75\,\mathrm{mJ/cm}^2$. The nonlinear transmission versus input fluence of the solution was fitted using Eq. (1) as well (Fig. 2 inset). All the data are well fitted by $\sigma_{\mathrm{ex}} = 33 \times 10^{-18}\,\mathrm{cm}^2$, which is close to σ_t of $\sim 33 \times 10^{-18}\,\mathrm{cm}^2$ and σ_s of $40 \times 10^{-18}\,\mathrm{cm}^2$ of lead Pc dilute solutions [14]. Therefore, we conclude that MPc-doped LC cells can be as effective a nonlinear absorber as MPc dilute solution.

Figure 4 shows the transmitted power as the function of the input power in the cw measurements. The laser is unfocused with a beam diameter of 4 mm, and the sample is illuminated for 10 s for each data point. The threshold power, defined as the input power at which the output power begins to decrease, is 110 and 250 mW for Sample 1 and Sample 2, respectively; for completeness, a pure twisted LC cell of 70 μm thickness has been tested, and there is no polarization switching effect observed using the same experimental procedure. For smaller beam size, the power threshold is reduced correspondingly. For example, using the same measurement procedure, the threshold for Sample 1 with another unfocused 532 nm laser with a beam diameter of 1.5 mm is about 30 mW. The underlying mechanism could be laser-induced LC molecular axis reorientation (assisted by dye) and/or order parameter modifications, from whence the LC cell stops rotating the polarization direction of the light, showing that the crossed polarizer pair can switch off light effectively as shown in Fig. 4 [10]. This polarization switching process can operate at microsecond speeds for higher input intensities [11].

To further investigate the cw configuration, we made another composite, using the dye EUT-57, at roughly 0.76% weight ratio in 5-CB and placed it in a 70 μm LC cell with alignment layers and orientation as described above. The threshold power in this case is 25 mW as shown in Fig. 5; a picture of the fabricated cell is shown in the inset. With a smaller beam size, the power threshold is reduced. For example, with a focused beam (diameter of 80 μm), the power threshold was reduced to about 1.5 mW, indicating that very low power operation is possible with further optimization.

In conclusion, we have presented RSA and polarization switching effects in one sample of a nonlinear absorber dye (PbTCPc) doped in nematic liquid

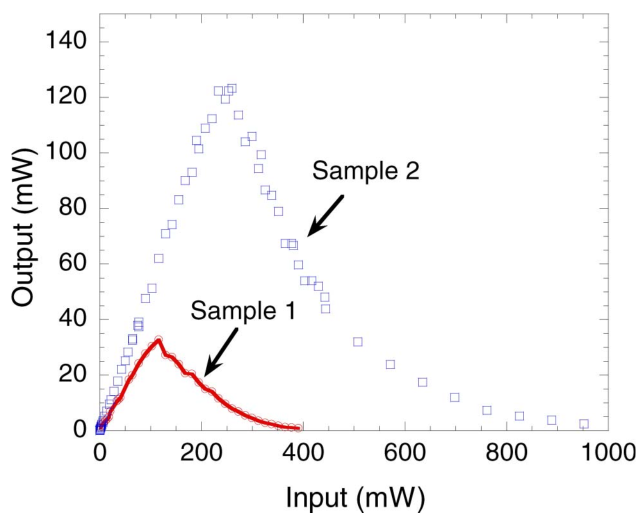

Fig. 4. (Color online) Transmitted power as a function of the input laser power for an unfocused laser.

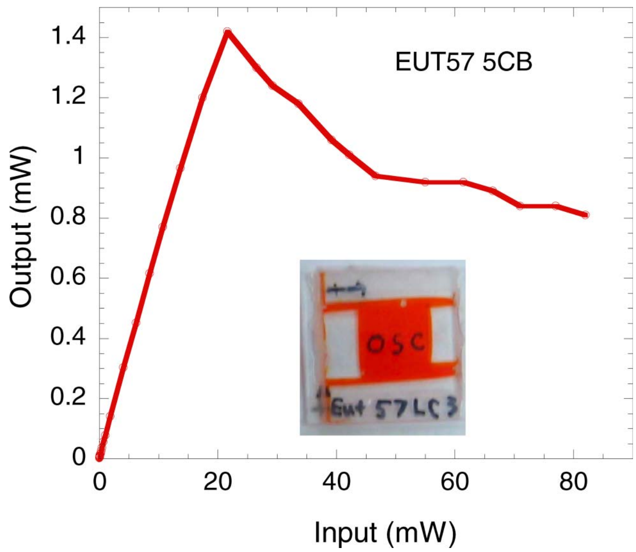

Fig. 5. (Color online) Transmitted power as a function of the input laser power for an unfocused laser for the EUT-57/5-CB composite; the inset shows a photograph of the sample.

crystals and have further investigated cw operation in another composite of EUT-57 and LC. The PbTCPc device works for both nanosecond pulses as well as cw and provides a promising approach to fabricating passive all-optical switches for multiple-time-scale lasers.

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